

Supporting Information

Lewis Acid-Assisted Detection of Nerve Agents in Water

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A. Synthesis and Characterization of Salen(^tBu)AlBr (SAB-1) (I)

A rapidly stirred solution of Et₂AlBr in toluene, prepared *in situ* by the redistribution of triethylaluminum (0.75 g, 6.57 mmol) and aluminum(III) bromide (0.89 g, 3.34 mmol), was combined with a solution of salen(^tBu)H₂ (5.0 g, 10.15 mmol) in toluene by cannula. The reaction mixture was refluxed for 8 h and filtered. The volatiles were removed under vacuum from the clear yellow filtrate to give a yellow microcrystalline solid which was purified by recrystallization from toluene. Yield: 4.8 g (79.20 %). mp: 330-332°C. ¹H NMR (CDCl₃): δ 1.48 (s, 18H, C(CH₃)₃), 1.72 (s, 18H, C(CH₃)₃), 3.93 (m, 4H, NCH₂), 7.35 (d, 2H, PhH), 7.43 (d, 2H, PhH), 8.56 (s, 2H, N=CH). IR (KBr; cm⁻¹): 2962 (m), 2905 (w), 2866 (w), 1648 (s), 1628 (s), 1544 (m), 1475 (m), 1444 (m), 1421 (w), 1390 (w), 1361 (w), 1310 (w), 1257 (w), 1180 (w), 867 (w), 845 (m), 816 (w), 786 (w), 756 (w), 608 (m), 586 (w). MS (EI, positive): *m/z* 597 (M⁺, 8%), 517 (M⁺ - Br, 100%).

B. Electro-Spray Mass Spectroscopy

1. Procedures and Instrumentation

Compound **I** was prepared as described in Section A. Compound **I** transfer to glass tube with Teflon cap under nitrogen atmosphere in an inert-atmosphere glovebox. Then glass tubes were sealed in fire proof air sealed Aluminum container and shipped to ECBC, MD.

At ECBC, compound **I** was used as received. It was dissolved in isopropanol at a stock concentration of 4 mg/mL, and diluted further to make standards. The samples were prepared by mixing (by volume) 10 µl of the stock solution with 100 µl of isopropanol, 10 µl of 0.5 M ammonium acetate solution in water, and 1-10 µl of acid or G agent standards. The final concentration of compound **I** was 0.55 mM. This concentration was not optimized, and a lower concentration could decrease the amount of dimer formation.

The solution of 0.5 M ammonium acetate buffer was used to exchange Br⁻ for acetate anions, and to provide a buffer for electrospray mass spectroscopy. Solutions of analyte acid or G agents were used at various concentrations.

Samples were analyzed on a ThermoFinnigan TSQ Quantum triple quadrupole mass spectrometer by flow injection at 5-50 µl/min with an electrospray ion source with default conditions and tuning, and using nitrogen drying gas. The spectrometer was calibrated to unit mass. Samples were analyzed in less than one hour after preparation.

2. Mass Spectra

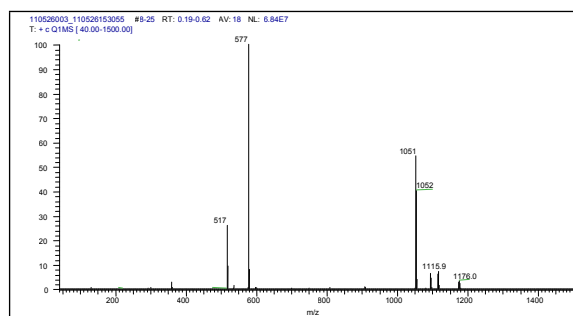


Figure S1

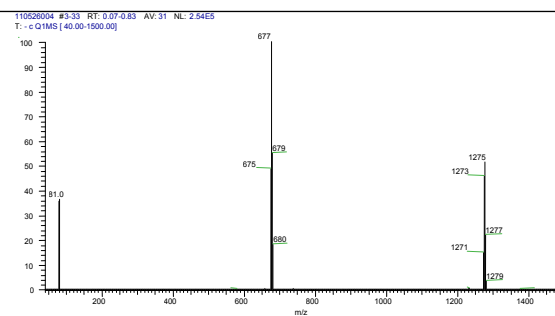


Figure S2

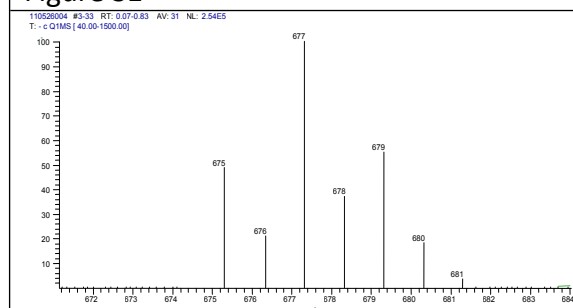


Figure S2 (insert 1)

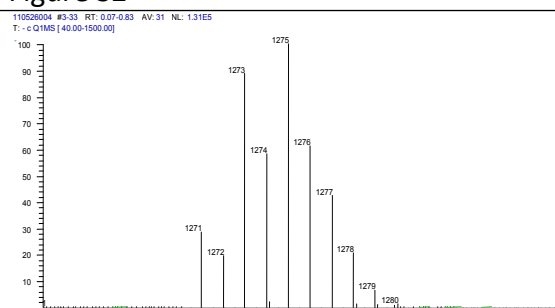


Figure S2 (insert 2)

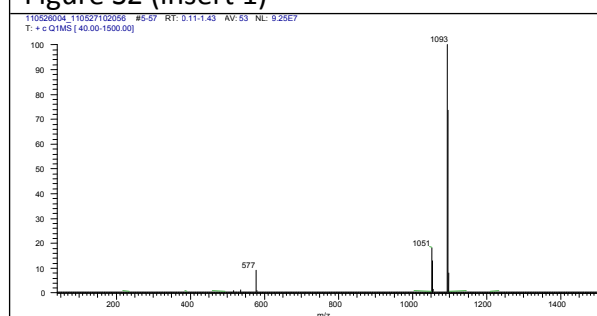


Figure S3

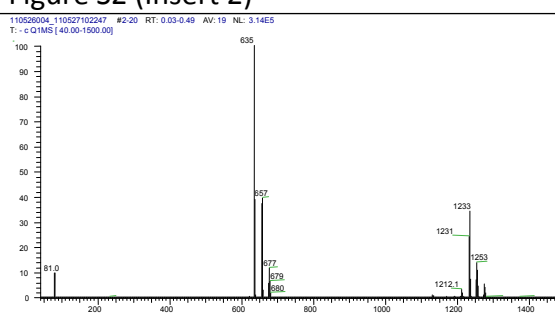


Figure S4

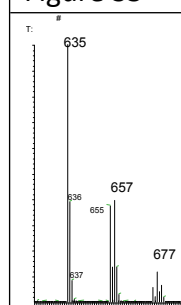


Figure S4 (insert 1)

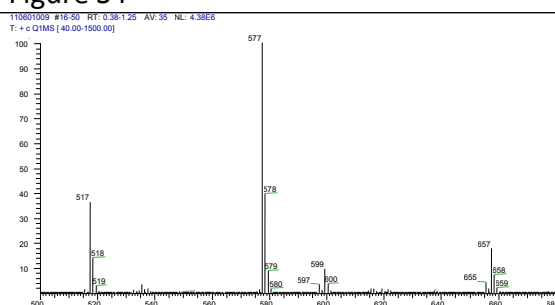


Figure S5

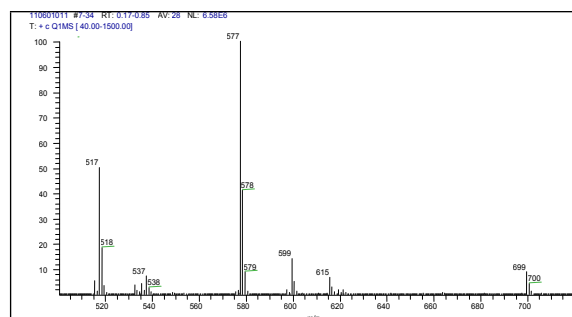


Figure S6

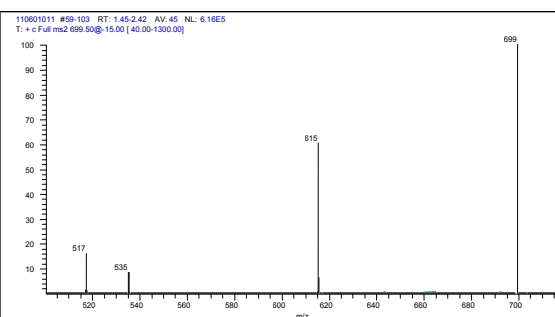


Figure S7

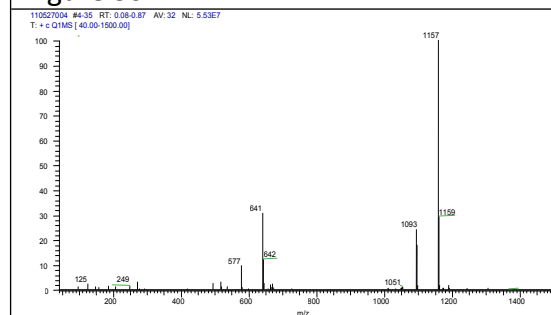


Figure S8

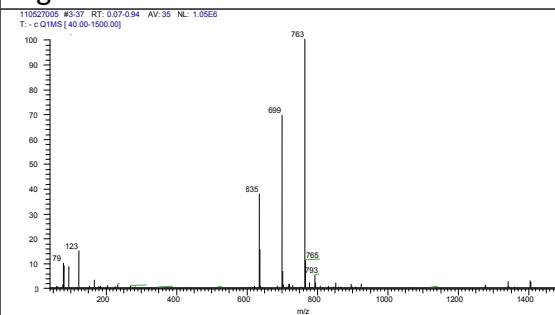


Figure S9

Table S1. Mass Numbers for each compound formed in a sequence of reactions leading to formation of Lewis acid-base compounds between Salen(^tBu)Al and the nerve agents (Scheme 1).

Compound	Formula	MW
1	Salen(^t Bu)AlBr	597.61
2	[Salen(^t Bu)Al(H ₂ O) ₂]Br	633.64
3	Salen(^t Bu)Al(OAc)	576.75
4	[Salen(^t Bu)Al(GB)] ⁺	657.79
5	[Salen(^t Bu)Al(GD)] ⁺	699.87
6	[Salen(^t Bu)Al(EMPA)] ⁺	641.78

C. Computational Study

The program package G09[1] was used for optimizations, frequency calculations, and solvation calculation. Complexes were optimized and frequencies calculated at the M05-2X/6-31+G(d) level while implicit solvation in water was modeled with SMD/B3LYP/6-31+G(2d,p). Estimated free energies of reaction were computed directly from SMD total energies. When free energies were computed with zero-point energies, integrated heat capacities and entropies using the equation $\Delta G(\text{aq}, 298\text{K}) = \Delta G(\text{g}, 298\text{K}, \text{M05-2X/M05-2X/6-31+G(d)}) + \Delta G(\text{sol}, \text{SMD/B3LYP/6-31+G(2d,p)})$, the resulting free energies of reaction agreed to within one kcal/mol.

Table S2. Total Free Energies of Species Calculated with SMD Implicit Solvation Modeling in Water (SMD/B3LYP/6-31+g(2d,p)) with Geometries Optimized at the M05-2X/6-31+G(d) Level

	Molecule		Energy	
	SalenAl ⁺		-1120.638750	
	Salen(Me)Al ⁺		-1277.922009	
	H ₂ O		-76.452140	
	Ac ⁻		-228.664497	
	P(O)(Me)(OMe)F		-671.607240	
	P(O)(Me)(OEt)OH		-686.909971	
	P(O)(Me)(OCHMe ₂)F		-750.252232	
	P(O)(Me)(OCH(Me)(ⁱ Pr))F		-828.884112	
	P(O)(Me)(OCH(Me)(^t Bu))F		-868.199914	
	Compound		L=Salen	L=Salen(Me)
a.	LAl(Ac)		-1349.355794	-1506.636759
b.	[LAl(H ₂ O)] ⁺		-1197.121708	---
c.	[LAl(H ₂ O) ₂] ⁺		-1273.584542	---
	[LAl(P(O)(Me)(OR)(X))] ⁺			
	R	X		
d.	Me	F	-1792.279046	-1949.560477
e.	CHMe ₂	F	---	-2028.206676
f.	CH(Me) ⁱ Pr	F	---	-2106.837795
g.	CH(Me) ^t Bu	F	---	-2146.153714
h.	Et	OH	-1807.587409	---

Reference:

[1] Gaussian 09, Revision D.01, M. J. Frisch, G. W. Trucks, H. B. Schlegel, G. E. Scuseria, M. A. Robb, J. R. Cheeseman, G. Scalmani, V. Barone, B. Mennucci, G. A. Petersson, H. Nakatsuji, M. Caricato, X. Li, H. P. Hratchian, A. F. Izmaylov, J. Bloino, G. Zheng, J. L. Sonnenberg, M. Hada, M. Ehara, K. Toyota, R. Fukuda, J. Hasegawa, M. Ishida, T. Nakajima, Y. Honda, O. Kitao, H. Nakai, T. Vreven, J. A. Montgomery, Jr., J. E. Peralta, F. Ogliaro, M. Bearpark, J. J. Heyd, E. Brothers, K. N. Kudin, V. N. Staroverov, R. Kobayashi, J. Normand, K. Raghavachari, A. Rendell, J. C. Burant, S. S. Iyengar, J. Tomasi, M. Cossi, N. Rega, J. M. Millam, M. Klene, J. E. Knox, J. B. Cross, V. Bakken, C. Adamo, J. Jaramillo, R. Gomperts, R. E. Stratmann, O. Yazyev, A. J. Austin, R. Cammi, C. Pomelli, J. W. Ochterski, R. L. Martin, K. Morokuma, V. G. Zakrzewski, G. A. Voth, P. Salvador, J. J. Dannenberg, S. Dapprich, A. D. Daniels, Ö. Farkas, J. B. Foresman, J. V. Ortiz, J. Cioslowski, and D. J. Fox, Gaussian, Inc., Wallingford CT, 2009.